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(12) # EUROPEAN PATENT APPLICATION

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(54) **Glass composition and use.**

(57) A glass composition capable of being spun into fibres has the following components expressed as weight percent : SiO_2 - 66 to 73 ; Al_2O_3 - 0.85 to 5 ; R_2O (= Na_2O + K_2O) - 14 to 17.5 ; CaO - 6.5 to 12 ; and SiO_2 + A_2O_3 - 69 to 74. The composition is free of boric oxide and consequently avoids pollution difficulties associated with that compound, yet it can be used in high temperature spinners to produce durable fibres.

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This invention relates to a boric oxide free glass composition capable of being spun into fibres, it also relates to a method of spinning compositions according to the invention in a spinner made from a mechanically alloyed or oxide dispersion strengthened alloy and to glass fibre insulation produced from the compositions according to the invention.

Glass compositions are known for use in the technique of fiberizing glass using a centrifugal spinner. The compositions have customarily incorporated boric oxide in order to give them temperature/viscosity characteristics that will enable the glass to pass freely through orifices in the centrifugal spinner wall at a temperature sufficiently low to prevent excessive corrosion and erosion of the spinner. A problem with the use of boric oxide is that boron is volatile and may escape from the glass melting tank to cause pollution problems. Furthermore it tends to condense on regenerators thereby fouling them up and preventing use of such devices to improve the thermal efficiency of fuel fired glass melting tanks.

GB 2 041 910 proposes the reduction or elimination of boric oxide with a consequent rise in liquidus temperature and high levels of alumina or baria. These reduced boric oxide compositions are acknowledged to be virtually impossible to fiberize on an industrial basis by the prior art spinning techniques. A technique involving the use of a novel spinner shape is proposed, but, in practice, the corrosion of such a spinner when fabricated from conventional alloy is unacceptably high. Also the glass compositions according to this patent have unacceptably low durability.

US Patent 4 402 767 proposes a novel spinner fabrication process to produce a mechanically alloyed or oxide dispersion strengthened alloy by a combination of warm working, annealing and hot forming processes. Such spinners are claimed to have excellent resistance against molten glass attack and are said to be capable of producing glass fibres and mineral wool at temperatures as high as 1315°C. No details of glass fibre production are given in the specification.

The problem has been to identify boron free glass compositions which have the required durability and can be used in high temperature spinners such as those described in US 4 402 767. Although the absence of boric oxide gives rise to a deterioration in the aqueous durability of the glass, we have identified a range of compositions for which the durability is satisfactory.

According to the present invention a boric oxide free glass composition capable of being spun into fibres, comprises the following components, expressed as weight percent:

SiO_2	66-73
Al_2O_3	0.8-5
$R_2O = Na_2O + K_2O$	14-17.5
CaO	6.5-12
$SiO_2 + Al_2O_3$	69-74

Such glasses have a viscosity of 1000 poise or less at temperatures up to about 1200°C and a liquidus at least 130°C below the 1000 poise temperature.

The composition may also contain : 0-2% Fe_2O_3; 0-5% MgO; 0-0.6% SO_3, all expressed as weight percent.

Preferably the components are present in weight percentages within the following ranges:

SiO_2	67-72.4
Al_2O_3	1-4
R_2O	14.5-17
K_2O	0.5-2
Na_2O	13.5-16.5
CaO	7-11.2
Fe_2O_3	0.1-2.5
MgO	0.2-4.4
$SiO_2 + Al_2O_3$	70-73.7

Most preferably the components are present in weight percentages within the following ranges

SiO_2	67-70
Al_2O_3	2-4
Na_2O	14-15.5
K_2O	0.5-1.5
MgO	3-4.5
CaO	7-8.5
Fe_2O_3	0.3-2
SO_3	0-0.3
$SiO_2 + Al_2O_3$	70-72
$Na_2O + K_2O$	15-16.5

A high level of Na_2O is needed to give a low liquidus temperature but the preferred narrow range of MgO allows the Na_2O to be kept to a minimum so optimising durability while maintaining liquidus at least 160 centigrade degrees below the 1000 poise viscosity temperature, which is advantageously below 1170°C.

The invention will now be described with reference to the following non-limiting examples 1-28. Low levels of SO_3, K_2O and Fe_2O_3 are recorded as a minimum in these examples. In fact they are only present at the lower levels as impurities in the raw materials and do not make a significant contribution to the properties of the glass fibres. Details of the examples and durability tests are given in the Table. It should be noted that Example 18 falls outside the scope of the present invention as its low level of alumina renders it insufficiently durable.

There is no established international test procedure for assessing the suitability of a glass for glass fibre insulation applications. It has become the practice to use the laboratory ware test of ISO 719 as it gives a useful guide to the aqueous durability and weathering resistance of the glass. In this test 2g of glass grains are treated with distilled water for 60 mins at 98°C and the extracted alkali titrated against 0.01 M HCL. The durability is described in terms of the alkali extracted per gram of glass as calculated from the acid required to neutralise. The relevant classes for glass wool are ISO Class 3 - from 62 to 264 micrograms of alkali per gram; and Class 4 - from 265 to 620 micrograms per gram. Glass wool is preferably in Class 3 but a good Class 4 may be acceptable because the performance of the insulation is a function of both glass and resin binder, and binders are available for use with higher release glasses. A class 3 rating is good and a class 4 rating is acceptable, but not as good.

Table 1

Example	1	2	3	4	5	6	7	8
SiO2	70	69	68	67	70	69	67	67
Al2O3	1	2	3	4	3	3	3	3
SiO2+Al2O3	71	71	71	71	73	72	70	70
Fe2O3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
CaO	8	8	8	8	8	8	8	9
MgO	4	4	4	4	4	4	4	4
Na2O	15.5	15.5	15.5	15.5	13.5	14.5	16.5	15.5
K2O	1	1	1	1	1	1	1	1
R2O	16.5	16.5	16.5	16.5	14.5	15.5	17.5	16.5
SO3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Tlog3	1146	1150	1155	1159	1191	1173	1136	1142
liquidus	952	964	982	1002	1012	1002	980	1018
ugR2O/g	307	270	260	248	186	251	406	285
Class	4	4	3	3	3	3	4	4

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Table 1

Example	9	10	11	12	13	14	15	16
SiO2	69	68.5	69	68	72.4	70	68	68
Al2O3	3	3	3	3	1.3	3	4	3
SiO2+Al2O3	72	71.5	72	71	73.7	73	72	71
Fe2O3	0.3	0.3	0.3	1.3	0.1	0.3	0.3	1.9
CaO	7	8	7.5	7.5	11.2	8.3	7.5	8
MgO	4	4	4	4	0.2	3.9	3.5	3.9
Na2O	15.5	15	15	15	14	13.5	15.5	14
K2O	1	1	1	1	0.5	0.9	1	1
R2O	16.5	16	16	16	14.5	14.4	16.5	15
SO3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Tlog3	1166	1163	1169	1163	1170	1195	1158	1170
liquidus	950	990	966	1000	1018	1018	996	1026
ugR2O/g	298	258	259	253	286	231	256	195
Class	4	3	3	4	4	3	3	3

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Table 1

Example	17	18	19	20	21	22	23	24
SiO2	68.5	71	68	69	68	67	66	66
Al2O3	3	0	3	3	3	3	3	4
SiO2+Al2O3	71.5	71	71	72	71	70	69	70
Fe2O3	0.3	0.3	0.3	0.3	1.3	2.3	3.3	2.5
CaO	7.6	8	8	7.5	7.5	7.5	7.5	7.8
MgO	4.4	4	4	4	4	4	4	3
Na2O	15	15.5	15.5	15	15	15	15	15.5
K2O	1	1	1	1	1	1	1	1
R2O	16	16.5	16.5	16	16	16	16	16.5
SO3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Tlog3	1165	1142	1154	1170	1164	1157	1150	1155
liquidus	1006	940	981	974	994	1002	1024	1010
ugR2O/g	251	474	251	259	253	236	239	240
Class	3	4	3	3	3	3	3	3

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Table 1

Example	25	26	27	28
SiO2	66	70	69.5	70.5
Al2O3	4	2	2	3
SiO2+Al2O3	70	72	71.5	73.5
Fe2O3	2.5	0.5	0.5	0.3
CaO	6.8	8.5	8.5	8
MgO	4	4	4	4
Na2O	15	14.5	14	13
K2O	1.5	0.5	1.5	1
R2O	16.5	15	15.5	14
SO3	0.2	0	0	0.2
Tlog3	1164	1166	1165	
liquidus	1014	1006	1005	
ugR2O/g	206	261	229	186
Class	3	3	3	3

Claims

1. A boric oxide free glass composition capable of being spun into fibres, comprising the following components expressed as weight percent:

SiO_2	66-73
Al_2O_3	0.8-5
$R_2O = Na_2O + K_2O$	14-17.5
CaO	6.5-12
$SiO_2 + Al_2O_3$	69-74

2. A glass composition according to claim 1, further comprising the following components expressed as weight percent:

Fe_2O_3	0-2
MgO	0-5
SO_3	0-0.6

3. A glass composition according to claim 1 or 2, wherein the components are present in weight percentages within the following ranges:

SiO_2	67-72.4
Al_2O_3	1-4
R_2O	14.5-17
K_2O	0.5-2

Na_2O	13.5-16.5
CaO	7-11.2
Fe_2O_3	0.1-2.5
MgO	0.2-4.4
$SiO_2 + Al_2O_3$	70-73.7

4. A glass composition according to claim 3, wherein the components are present in weight percentages within the following ranges:

SiO_2	67-70
Al_2O_3	2-4
Na_2O	14-15.5
K_2O	0.5-1.5
MgO	3-4.5
CaO	7-8.5
Fe_2O_3	0.3-2
SO_3	0-0.3
$SiO_2 + Al_2O_3$	70-72
$Na_2O + K_2O$	15-16.5

5. An insulating glass fibre production process including the spinning of molten glass at a high temperature in a spinner made from a mechanically alloyed or oxide dispersion strengthened alloy to produce fibres having a composition according to any preceding claim.

6. Insulating glass fibres having a composition according to any one of claims 1 to 4.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 4660

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X Y	EP-A-0 399 320 (BAYER AG.) * abstract *	1-4,6 5	C03C13/00 C03C3/087
D,X Y	US-A-4 203 746 (J.A. BATTIGELLI ET AL.) * table IV *	1-4,6 5	
X Y	CHEMICAL ABSTRACTS, vol. 97, no. 20, 1982, Columbus, Ohio, US; abstract no. 167698Y, M. CZAJA ET AL.: 'Results of the selection of technological and design parameters for production of glass fibers' page 299 ; * abstract *	1-4,6 5	
D,Y	US-A-4 402 767 (J.W. HINZE ET AL.) * the whole document *	5	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
C03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	08 SEPTEMBER 1992	REEDIJK A.M.E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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